Correlation between Quantized Electronic States and Oscillatory Thickness Relaxations of 2D Pb Islands on Si(111)-(7 × 7) Surfaces

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Two-dimensional lead (Pb) islands of varying heights have been grown on the Si(111)-(7 × 7) surface at low temperature. Individual islands are investigated concurrently with real-space and local-probe scanning tunneling microscopy and spectroscopy. Quantum size effects, manifested in the formation of new electronic bound states, redistribution of surface charge density, and oscillatory relaxations in island thickness are found to be perfectly correlated to each other.

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Thin metal films and small quantum dots have a wide range of applications in modern technologies. Quantum size effects (QSE) begin to appear as the size of a small object becomes comparable to the de Broglie wavelength of electrons confined in it. These effects, though originated from the electron confinement, can have a profound effect on various nanoscale physical properties. For instance, Schulte [1] earlier calculated the film thickness dependence of electron densities, potentials, and work functions for freestanding metal films and found oscillations in all these quantities. This prediction was experimentally studied later by different techniques such as tunneling current [2], work function change [3], electrical resistivity [4], and photoemission spectroscopy [5,6]. In addition, when the effect of discrete lattice was studied for the Al(111) slabs, both Feibelman [7] and Batra *et al.* [8] concluded that structural variations could be related to the QSE also. The variation was indeed detected by a He scattering experiment for the Pb/Ge(100) system [9]. All these findings exemplify the unusual behavior of thin films varying with their thickness. However, clear experimental evidence directly relating quantized electronic states to interlayer relaxations of individual islands has not been reported.

Intuitively, one would like to grow a thin metallic film on an insulator or semiconductor substrate so that electrons in the film will be bound on one side by vacuum and the other by the interface. Unfortunately, in practice it is difficult to grow metal films on insulators or semiconductors in a layer-by-layer fashion. Instead, discontinuous films with varying thicknesses are usually formed. Previous measurements of the QSE by broad beam techniques [2–6,9], therefore, have one common drawback—those results are the averages over a large number of islands with different heights. Although the QSE can still be detected due to the discontinuous nature in film thickness, it is difficult to establish directly their correlations without some ambiguities.

The first observation of the QSE for individual Pb islands grown on the Si(111) surface was made by Altfeder *et al.* [10] employing both scanning tunneling microscopy (STM) and spectroscopy (STS). The same Pb/Si(111) system is chosen here because Pb possesses a nearly free-electron Fermi surface [11], which facilitates the assignment of quantum numbers to the quantized states of the films. We have also extended the detection of quantum states toward thinner films and have clearly established a correlation between the electronic property and the thickness of an individual island.

Pb was *in situ* deposited onto the Si(111)-(7 × 7) surface with the flux of ~0.16 monolayer (ML) per minute. A coverage of Pb film less than 5 ML deposited at a temperature between 170 and 250 K typically results in the formation of islands of four to nine atomic layers in height above a wetting layer [Fig. 1(a)]. This layer consumes 2 ML of Pb according to our own estimate and also Ref. [12]. Previous results [4,12] indicate the top faces of these islands are the (111). Figure 1(b) represents a height distribution of these islands. The peak 0 marks the height of the wetting layer, and the rest of the peaks correspond to 4, 5, 7, and 9 atomic layers, respectively [13]. The growth of islands with sharp edges, flattop, and well-defined height thus calls for a new growth mechanism—"electronic growth" based on the QSE [14]. The critical and magic thicknesses found here imply that the growth process has the same origin. Further details of our study of growth behavior for this system will be published later [15].

Electronic properties of an island can be directly correlated to its thickness. This is done by simultaneously performing a topographic and a spectroscopic (dI/dV) imaging. As the electronic wave functions normal to the plane (defined as the z direction) of the islands are modified by the imposed boundary conditions, only standing wave states are allowed to exist. The corresponding density of states displays a stepwise increase with the energy, which should be detectable with STS. Figure 2 displays some dI/dV spectra taken on the islands of

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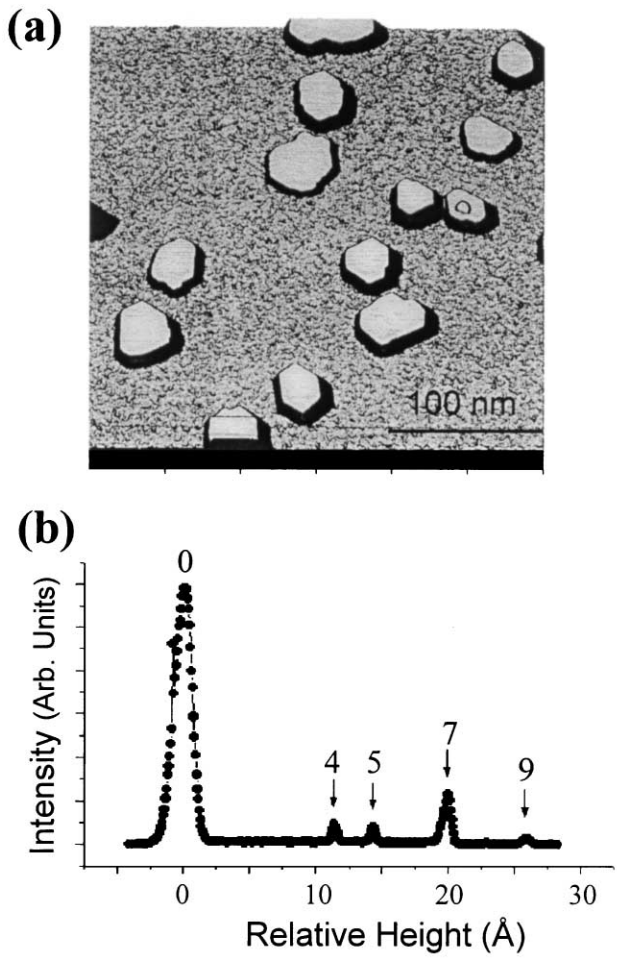

FIG. 1. (a) Topographic STM image (300 nm × 300 nm), taken with the sample bias of 2 V, of Pb islands grown on Si(111) substrate at 200 K and coverage of 3.2 ML. (b) The distribution intensity of these islands as a function of their thicknesses.

different height. These spectra exhibit some peaks at the onsets of new emerging subbands. The Fermi level is indicated with a thick line across the center. Thus, down-pointing arrows mark the onsets of the highest occupied subbands (HOS) and up-pointing arrows the lowest unoccupied subbands (LUS). The short-dotted lines mark the middle positions between the two kinds of arrows. The energy separation (Δ) between HOS and LUS is a function of the island thickness (H). Their relation is $\Delta = \pi\hbar V_F/H$, where $\hbar$ is the Plank's constant, and V_F is the Fermi velocity. In the previous work [10], a Fermi velocity of $V_F = 1.9 \times 10^8$ cm/s is obtained by fitting a straight line to their data from layer 8 to layer 15. Here we find our data (from layer 4 to layer 9) can fit into the line as well [Fig. 3(a)]. The extrapolated $1/\Delta$ line intersects the height axis at -3 (layers) [10], implying the actual thickness of the quantum well should add two for the wetting layer and one for penetration of electron wave functions across the boundaries of the film. A simple sketch to illustrate this geometry is drawn in Fig. 3(b). The total width (w_N) of the quantum well is estimated to

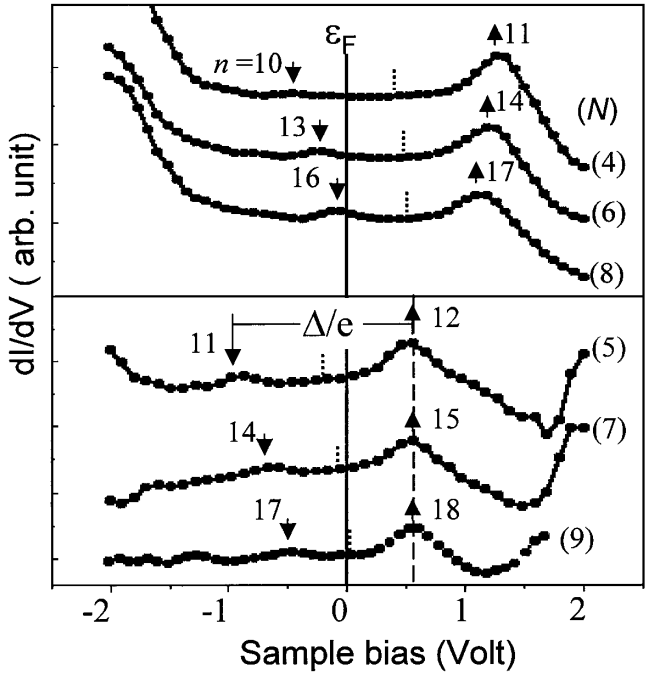

FIG. 2. A series dI/dV spectra taken on individual islands of varying thickness numbered in parentheses from $(N) = (4)$ to (9). The lower case n indicates the quantum number associated with the quantized state. The HOS are marked with point-down arrows and the LUS are marked with point-up arrows. The short-dotted lines mark the middle positions between the HOS and the LUS.

be the sum of a half of the interface spacing ($d/2$), the wetting layer ($2d_0$), the measured thickness of the N-layer island (t_N), and the extension towards the vacuum ($d_0/2$), i.e., $w_N \approx d_i/2 + 2d_0 + t_N + d_0/2 \approx t_N + 3d_0$.

Previous measurements of the quantum size effects obtained by averaging over the islands of varying heights cannot assign a specific quantum number to any quantized state. In this study, every spectrum is directly related to the island thickness and thus renders the possibility. The realization of a still peak, marked with a dashed line, in the spectra of $N = 5$, 7, and 9 at 0.56 eV above the Fermi level (Fig. 2) (also referring to Fig. 3 of Ref. [10] for $N = 9$, 11, 13, and 15) is the consequence of a constant state at $k = 3\pi/2d_0 = n\pi/w_N \approx n\pi(N + 3)d_0 \Rightarrow 2n \approx 3(N + 3)$; here n is a quantum number. This constant state can be inferred from the Fermi level measurement [2,11], where along the [111] direction it falls near to $\pi/2d_0$ of the second band in the reduced zone scheme, which is equivalent to $3\pi/2d_0$ for the free-electron model. Though one might argue that N could have an uncertainty of ± 1, to satisfy the above equation, however, N has to be an odd integer. Therefore, for $N = 5, 7$, and 9, the corresponding quantum numbers for the fixed states can be safely determined as $n = 12, 15$, and 18. Other quantized states can then be numbered accordingly. This assignment is helpful later in describing the correlation of the bound electronic states to a thickness oscillation.

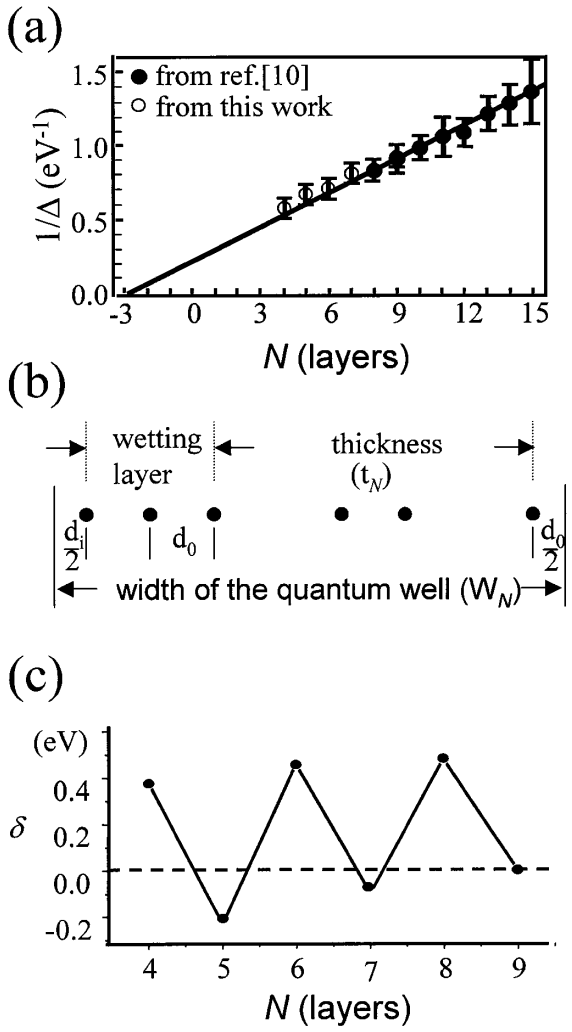

FIG. 3. (a) The inverse of energy separation between the HOS and the LUS as a function of the island thickness. The solid line is a fit to the data with $V_F = 1.9 \times 10^8$ cm/s. (b) A sketch to illustrate the actual width of the quantum well (see text). (c) The energy separation s(δ) from the middle positions of the HOS and the LUS to the Fermi level as a function of island thicknesses.

In Fig. 2, the middle position between the energies of HOS (E_{HOS}) and LUS (E_{LUS}) is marked with a dotted line. Inspecting their distances (δ) from the Fermi level, here $\delta = (E_{\mathrm{HOS}} + E_{\mathrm{LUS}})/2 - E_F$, those for the odd-numbered curves are much closer than those of the even numbered, and if plotted against the island thickness, they also exhibit a bilayer oscillation as described in Fig. 3(c). It suggests that the odd-numbered layers should have a higher concentration of surface charge density than their counterparts, which in turn makes the surface energy of the odd-numbered lower. This may be the reason why islands with odd-numbered layers are more abundant [see Fig. 1(b)], and this phenomenon can be demonstrated with Fig. 4(a) in a dynamical fashion. The base island here is $N = 5$ and layers of $N = 6$ and 7 are on top of it. At 200 K, the islands of six-layer height are unstable, and with time (from frame 1 to frame 3) they merge into the seven-layer island surrounding the perimeter. In addition, the varying surface electronic properties will also cause the work function to vary and invoke the ion cores into relaxing to counteract the change in work function.

To further elaborate on this point, we need to examine the bilayer oscillation observed in Fig. 4(b). In this figure, the deviation from the ideal thickness, defined as $\Delta t = t_N - N \times 2.85$ Å, for various islands [such as those in Fig. 1(a)] are plotted against their layer numbers and connected by solid lines. The amplitude of the variation measured at sample bias of 2 V is very large and can involve both structural and electronic contributions. In fact, the electronic interference phenomenon in quantum wedge has been demonstrated [10]. In order to confirm the possible existence of the oscillation in real height, we first examine the variation in apparent height for various biases. For negative sample biases, the amplitudes of oscillation are about the same but change very much for positive biases larger than 3 V and smaller than 1 V. However, in spite of the difference in oscillation amplitude, the trend never reverses, which legitimately implies existence of the structural oscillation. Furthermore, in Fig. 4(a) the height across the islands (indicated by the arrow) clearly displays an expansion between $N = 5$ and 6 as well as a contraction between $N = 6$ and 7 (referring to the line profile). The interlayer spacing exhibits a similar oscillatory dependence [dotted lines in Fig. 4(b)] with smaller amplitude. Since the I/V spectra taken on these islands are indiscernible with those on isolated islands of the same height, we must attribute this slight difference to an incomplete relaxation of the even-numbered islands, which may be caused by the existence of continuous strains at the interfaces of various tiers. This also confirms that the relaxation phenomena have penetrated the whole film.

The origin of contraction and expansion in the film thickness is attributed to the QSE through variation in surface charge distribution that also exhibits a bilayer oscillation [Fig. 3(c)]. The Fermi wavelength (λ_F) along the (111) direction for the Pb crystal is 3.94 Å [4], and the addition of every $\lambda_F/2$ introduces a new quantum state. In Table I, islands of varying thickness (N layers) above the wetting layer and their corresponding effective widths (w_N) [16] of quantum well are tabulated. The last column displays the round-off integer values (n) of w_N divided by $\lambda_F/2$. Each n thus represents the quantum number for the highest occupied state in each film. Comparing these numbers with those in Fig. 2, we find a perfect agreement between them. Furthermore, we now reach a clear picture of why the thickness of an island will oscillate according to its layer number. A critical reason is because the film cannot grow infinitesimally in thickness. Once a thin film grows thicker, the newly introduced electrons tend to occupy the next bound state. In order to form a new bound state, the thickness of the film has to increase by an integer number of $\lambda_F/2$. Examining the relation between the interlayer spacing $d_0 = 2.85$ Å and Fermi half-wavelength $\lambda_F/2 = 1.97$ Å, we have $2d_0 \approx 3\lambda_F/2$, which implies that every bilayer growth of Pb can

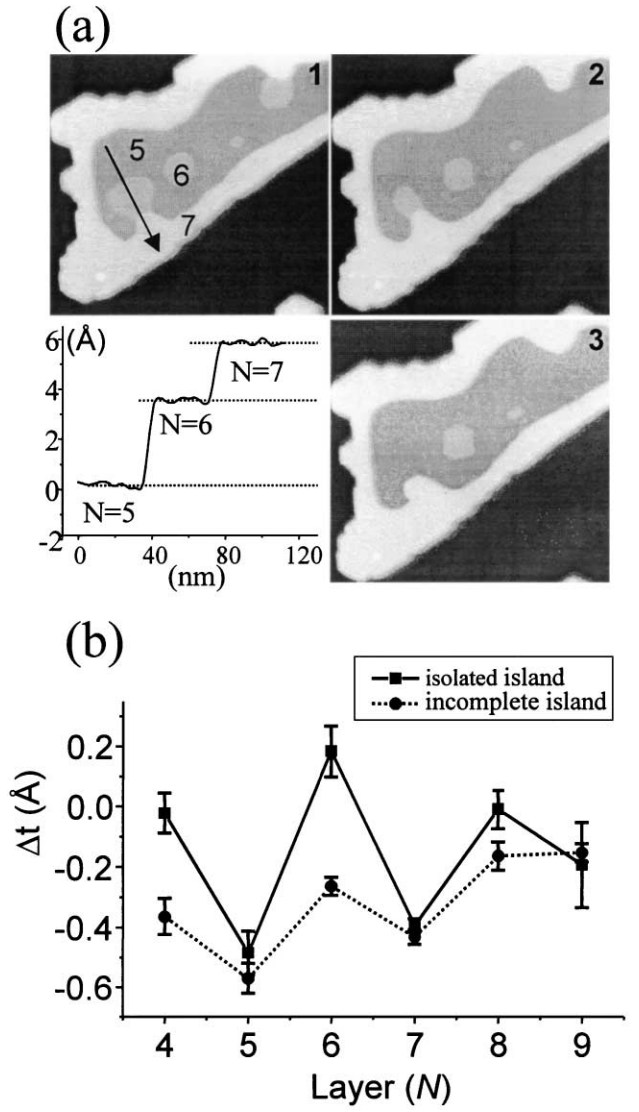

FIG. 4. (a) STM images (300-nm × 300-nm) of *in situ* growth of thin Pb films on an $N = 5$ island, taken with the sample bias of 2 V. The height profile is measured along the line island in frame 1. Frames 2 and 3 are images taken subsequently. (b) The deviation from the ideal island thickness (solid lines) measured from various individual islands and that (dotted lines) measured from an island of several tiers, such as the one in (a), as a function of the island thickness N, exhibiting an extraordinary oscillation.

accommodate about three new bound electronic states. Therefore, the increase of the quantum number will result in a sequence of one followed by two (referring to the n values in Table I) and the thickness of the growing film should thus relax accordingly. It is worth noting that, even with this primitive picture, a turn-around point happens at $N = 10$ (referring to Fig. 3 of Ref. [10]) can also be predicted.

In summary, we have investigated the physical properties of 2D Pb islands grown on Si(111) surfaces at low temperature. The quantized electronic states resulted from the finite thickness normal to the surface set off surface charge variation and structural relaxation of the island, and their correlation is clearly demonstrated with definitive assignment of the quantum numbers.

TABLE I. The overall width of quantum well (w_N) [16] and the round-off integers ($[n]$) defined as the division of w_N by the Fermi half-wavelength ($\lambda_F/2$) as a function of the Pb island layers (N) measured with respect to the wetting layer.

Layer (N)	W_N (Å)	$[n]$
4	20.15	10
5	23.00	11
6	25.85	13
7	28.70	14
8	31.55	16
9	34.40	17
10	37.25	18
11	40.10	20

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[16] Since the real thickness cannot be obtained by STM and the effective width (w_N) is likely varying with the islands of different height, we thus employ an estimation of $w_N \approx (N + 3)d_0 + 0.2$ Å. This is because the Fermi level of $N = 8$ is very close to its HOS ($n = 16$) and $n\lambda_F/2 \approx 31.55$ Å.